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# Discrete systems in thermal physics and engineering: a glance from non-equilibrium thermodynamics

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**Abstract** Non-equilibrium processes in Schottky systems generate by projection onto the equilibrium subspace reversible accompanying processes for which the non-equilibrium variables are functions of the equilibrium ones. The embedding theorem which guarantees the compatibility of the accompanying processes with the non-equilibrium entropy is proved. The non-equilibrium entropy is defined as a state function on the non-equilibrium state space containing the contact temperature as a non-equilibrium variable. If the entropy production does not depend on the internal energy, the contact temperature changes into the thermostatic temperature also in non-equilibrium, a fact which allows to use temperature as a primitive concept in non-equilibrium. The dissipation inequality is revisited, and an efficiency of generalized cyclic processes beyond the Carnot process is achieved.

**Keywords** Schottky systems · Contact quantities · Non-equilibrium entropy · Clausius inequalities · Adiabatical uniqueness · Embedding theorem · Accompanying processes · Thermodynamical stages · Dissipation inequality · Generalized cyclic processes · Efficiency

## 1 Preface: motivation

This tutorial paper which summarizes some known and some novel results of non-equilibrium thermodynamics concerning temperature and entropy is addressed to those who are interested in fundamentals of thermodynamics of non-equilibrium beyond the usual frame. One may be of the opinion that these fundamentals are well known [1, 2], but this impression is not true as can be seen by the following argumentation.

Temperature and entropy are well defined in thermostatics, that is the area of reversible "processes" which do not exist in reality (do not take them for quasi-static processes). But most of the thermal processes are irreversible: heat conduction, diffusion, friction, chemical reactions. The question arises: why in all these non-equilibrium items, the equilibrium temperature can be used successfully, especially since a non-equilibrium entropy is introduced? There is only one way to answer this question: a measurable non-equilibrium temperature has to be defined, and one has to search for conditions which allow to replace this non-equilibrium temperature exactly by the thermostatic equilibrium temperature (do not think of hypotheses as local equilibrium or endoreversibility).

In connection with the non-equilibrium entropy, the busy physicists have generated a lot of "non-equilibrium temperatures" with the shortcoming that these may not fit to the used thermometers. Thus, it was obvious, first

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Communicated by Andreas Öchsner.

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In memory of Joseph Kestin.

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to find a non-equilibrium temperature fitting to the thermometers and afterwards to define a non-equilibrium entropy. This is the contact temperature, the starting-point of this paper, whose aim is to elucidate the connection between temperature and non-equilibrium. The replacement of the non-equilibrium contact temperature by the thermostatic temperature needs some formal, but easy and clear procedures. Of course, several unfamiliar notations appear, such as embedding theorem, adiabatic uniqueness and thermal stage, but they all are transparent concepts of non-equilibrium thermodynamics. After some efforts, the elucidation shows up why and when in thermal physics the equilibrium temperature can be used exactly even in non-equilibrium.

## 2 Introduction

There are two kinds of describing thermodynamic phenomena phenomenologically: in field formulation or as a discrete system which also is called a Schottky system [3]. The field formulation is able to describe more details than the gross representation by a Schottky system. Both tools have their special realm of application: field formulation, if one can establish differential equations with corresponding initial and boundary conditions, and considering a discrete system in interaction with its environment [4], a situation which is frequent in thermal engineering because especially boundary conditions of possible differential equations are unknown. Here, this second case is considered using non-equilibrium thermodynamics of discrete systems.

First of all, one has to realize that non-equilibrium thermodynamics means that a non-equilibrium entropy and consequently also a non-equilibrium temperature have to be introduced [5] and that these quantities have to be consistent with thermostatics (equilibrium thermodynamics). There exists a detailed literature on non-equilibrium temperature [6], but the problem arises, if for such a formal non-equilibrium temperature also a thermometer exists or if this temperature is only an arithmetical quantity.

There is a huge variety of different thermometers [7,8] all measuring "temperature," but the concept of temperature is first of all only properly defined by thermal equilibrium. For elucidating this fact, we consider the simple example of a thermometer whose surface<sup>1</sup> has different zones of heat conductivities. Contacted with a non-equilibrium system, the measured "temperature" depends at the same local position on the orientation of such a "thermometer." Clear is that, this orientation sensitivity of the thermometer vanishes in equilibrium. A second example is a thermometer which measures the intensity of radiation which is composed of different parts of the spectrum. The measured "temperature" depends on the sensitivity distribution of the thermometer over the spectrum with the result, that different thermometers measure different "temperatures" at the same object.

For escaping these "thermometer-induced" difficulties, a theoretical definition of temperature in non-equilibrium is helpful as a remedy. Taking the usual abstract definitions of temperature  $T$  into account [8],

$$\text{discrete systems: } \frac{1}{T} := \frac{\partial S}{\partial U}, \quad \text{field formulation: } \frac{1}{T} := \frac{\partial s}{\partial u}, \quad (1)$$

also these definitions have their malices: First of all, a state space on which  $S$  or  $s$  are defined is needed, because the partial derivatives in (1) have no sense without it. Then, entropy  $S$  or entropy density  $s$  and internal energy  $U$  or internal energy density  $u$  are needed in equilibrium and out of it. And finally, the open question is, if there exists a thermometer which measures that temperature  $T$ .

To avoid all these uncertainties, a simple idea is the following: why not define a general concept of temperature which is valid independently of equilibrium or non-equilibrium and which is introduced into the theoretical framework by defining the RHSs of (1), thus determining the partial derivatives entropy over temperature

$$\frac{1}{\Theta} =: \frac{\partial S}{\partial U}, \quad \frac{1}{\Theta} =: \frac{\partial s}{\partial u} ? \quad (2)$$

If additionally  $\Theta$  is connected with a measuring instruction which "defines" the temperature  $\Theta$  experimentally, temperature comes from the outside into the theoretical framework and not vice versa [9–11]. Because  $\Theta$  will generally be defined independently of equilibrium or non-equilibrium, also  $S$  and  $s$  are according to (2) such generalized quantities.

That these concepts of non-equilibrium temperature and entropy are not only interesting with respect to theoretical considerations, but also to systems of engineering thermodynamics—discrete systems—is demonstrated in the sequel.

<sup>1</sup> The thermometer is here a discrete system which has a volume and a surface, as small as ever.

The paper is organized as follows: After this introduction, Schottky systems are revisited, state spaces and processes, the 1st and the 2nd law are considered, and the entropy time rate and accompanying processes are introduced. Non-equilibrium contact quantities such as temperature, enthalpy, and chemical potentials are defined. After a brief view at internal variables, a non-equilibrium entropy is established by use of the adiabatic uniqueness and the embedding theorem. The results are summed up in so-called thermodynamical stages of Schottky systems. The dissipation inequality and the efficiency of generalized cyclic processes are treated in the last two sections. The paper finishes with a summary.

### 3 Schottky systems

Numerous situations in thermal sciences can be described by the interaction of a discrete system, a Schottky system, with its environment [4, 12]. Here, the system is in non-equilibrium and the environment in equilibrium or also in non-equilibrium. For describing such a compound system consisting of the discrete system and its environment, two kinds of variables are needed: the state variables describing the states of the sub-systems (discrete system and environment) and the interaction variables describing the exchanges between the sub-systems [13, 14].

A system  $\mathcal{G}$ , described as undecomposed and homogeneous, which is separated by a partition  $\partial\mathcal{G}$  from its environment  $\mathcal{G}^\square$  is called a *Schottky system* [3], if the interaction between  $\mathcal{G}$  and  $\mathcal{G}^\square$  through  $\partial\mathcal{G}$  can be described by<sup>2</sup>

$$\text{heat exchange } \dot{Q}, \quad \text{power exchange } \dot{W}, \quad \text{and material exchange } \dot{\mathbf{n}}^e. \quad (3)$$

The power exchange is related to the work variables  $\mathbf{a}$  of the system

$$\dot{W} = \mathbf{A} \cdot \dot{\mathbf{a}}. \quad (4)$$

Here,  $\mathbf{A}$  are the generalized forces which are as well known as the work variables. Kinetic and potential energy are constant and therefore out of scope.  $\dot{Q}$  is measurable by calorimetry and the time rate of the mole numbers due to material exchange  $\dot{\mathbf{n}}^e$  by weight.

#### 3.1 State spaces and processes

A large state space  $\mathcal{Z}$  [13] is decomposed into its equilibrium subspace containing the equilibrium variables  $\mathbf{\Omega}$  and into the non-equilibrium part spanned by the variables  $\mathbf{\Xi}$  which describe non-equilibrium and which are not included in the equilibrium subspace

$$\mathbf{Z} = (\mathbf{\Omega}, \mathbf{\Xi}) \in \mathcal{Z}. \quad (5)$$

The *states of equilibrium*  $\mathbf{\Omega}$  are defined by time-independent states of an isolated Schottky system and are determined by the *Zeroth Law*: The state space of a thermal homogeneous<sup>3</sup> Schottky system in equilibrium is spanned by the work variables  $\mathbf{a}$ , the mole numbers  $\mathbf{n}$  and the internal energy  $U$

$$\mathbf{\Omega} = (\mathbf{a}, \mathbf{n}, U) \longrightarrow \mathbf{Z} = (\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi}). \quad (6)$$

A process is defined as a trajectory on the non-equilibrium state space,

$$\mathbf{Z}(t) = (\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi})(t), \quad t = \text{time}. \quad (7)$$

In equilibrium, the non-equilibrium variables  $\mathbf{\Xi}$  depend on the equilibrium ones  $\mathbf{\Xi}(\mathbf{\Omega})$  and (6)<sub>2</sub> becomes

$$\mathbf{Z}^{eq} = (\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi}(\mathbf{a}, \mathbf{n}, U)). \quad (8)$$

<sup>2</sup> • means "per time," but not necessarily a time derivative, <sup>e</sup> means external.

<sup>3</sup> That means: there are no adiabatical partitions dividing the interior of the discrete system into compartments.

This fact gives rise to introduce a projection  $\mathcal{P}$  of the non-equilibrium state  $\mathbf{Z}$  onto the equilibrium subspace [14] resulting in an equilibrium state  $\mathbf{\Omega}$

$$\mathcal{P}\mathbf{Z} = \mathcal{P}(\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi}) = \mathbf{Z}^{eq} = (\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi}(\mathbf{a}, \mathbf{n}, U)) = (\mathbf{\Omega}, \mathbf{\Xi}(\mathbf{\Omega})). \quad (9)$$

Because this projection can be performed for each non-equilibrium state of a process (7), the time is projected onto the equilibrium states<sup>4</sup> now equipped with a time, thus representing an "equilibrium process," a bit strange denotation because neither a "process" with progress in time takes place on the equilibrium subspace nor does it exist in nature. Such "processes" are called *reversible*

$$\mathcal{P}\mathbf{Z}(t) = \mathbf{Z}^{eq}(t) = (\mathbf{a}, \mathbf{n}, U, \mathbf{\Xi}(\mathbf{a}, \mathbf{n}, U))(t). \quad (10)$$

Consequently, reversible processes are trajectories on the equilibrium subspace generated by a point-to-point projection of non-equilibrium states onto the equilibrium subspace, thus keeping the "time" as path parameter of  $\mathbf{\Omega}(t)$  which is also denoted as *accompanying process*  $\mathbf{Z}^{eq}(t)$  [15] which is detailed considered in Sect. 7.3. Although not existing in nature, reversible processes serve as thermostatic approximation and as mathematical closing of the set of "real" (irreversible) processes which are defined as trajectories on the non-equilibrium state space.

### 3.2 The first law

Up to now, the internal energy was introduced in (6)<sub>1</sub> as one variable of the equilibrium subspace of a thermally homogeneous Schottky system. The connection between the time rate of the internal energy of the system and the exchange quantities through  $\partial\mathcal{G}$  is established by the *First Law*

$$\dot{U} = \dot{Q} + \mathbf{h} \cdot \dot{\mathbf{n}}^e + \dot{W} \quad (11)$$

which states that the internal energy  $U$  of the system should be conserved in isolated Schottky systems. The second term of the RHS of (11) originates from the fact that the heat exchange has to be redefined for open systems ( $\dot{\mathbf{n}}^e \neq \mathbf{0}$ ) [16].

The total heat exchange of open systems is composed of its conductive part  $\dot{Q}(\zeta)$  and of its convective part  $\zeta \cdot \dot{\mathbf{n}}^e$  which has to be defined by a special choice of  $\zeta$ . According to this split,  $\dot{Q}$  and  $\dot{\mathbf{n}}^e$  are independent of each other, but the conductive heat exchange depends on the definition of the convective one. The chain of reasoning by Rolf Haase [17] runs as follows: starting with the enthalpy  $H = U - \mathbf{A} \cdot \mathbf{a}$  of the discrete system and its time derivative

$$\dot{H} = \dot{U} - \mathbf{A} \cdot \dot{\mathbf{a}} - \mathbf{a} \cdot \dot{\mathbf{A}} = \mathbf{h} \cdot \dot{\mathbf{n}} \quad (12)$$

with the molar enthalpies  $\mathbf{h}$  of the chemical components in  $\mathcal{G}$ , the First Law (13)<sub>1</sub> writes by taking the split of the total heat exchange, (4) and (12) into account

$$\dot{U} - \mathbf{A} \cdot \dot{\mathbf{a}} = \dot{Q}(\zeta) + \zeta \cdot \dot{\mathbf{n}}^e = \mathbf{h} \cdot \dot{\mathbf{n}} + \mathbf{a} \cdot \dot{\mathbf{A}}. \quad (13)$$

The relation (13)<sub>2</sub> is also valid for the following special case

- (i) there are no chemical reactions  $\dot{\mathbf{n}} = \dot{\mathbf{n}}^e$ , (21),
- (ii) the conductive heat exchange vanishes, that means, system and environment have the same temperature,<sup>5</sup>
- (iii) the generalized forces  $\mathbf{A}$  (e.g., the pressure) are constant.

This special case enforces  $\zeta = \mathbf{h}$  according to (13). Consequently, the special formulation (11) of the First Law is established.

<sup>4</sup> t is the "slaved time" according to (10).

<sup>5</sup> This is a colloquial statement because the non-equilibrium temperature of the system is not defined yet.

### 3.3 Entropy time rate and second law

Considering a discrete system  $\mathcal{G}$ , a quantity  $\mathbf{J}$  of  $\mathcal{G}$  is called *balanceable*, if its time rate can be decomposed into an exchange  $\Psi$  and a production  $\mathbf{R}$

$$\dot{\mathbf{J}} = \Psi + \mathbf{R}, \quad \Psi = \Phi + \varphi \dot{\mathbf{n}}^e. \quad (14)$$

The exchange is composed of its conductive part  $\Phi$  and its convective part  $\varphi \dot{\mathbf{n}}^e$ .

Doubtless, a non-equilibrium entropy of a Schottky system is a balanceable quantity.<sup>6</sup> Presupposing that the power exchange does not contribute to the entropy rate, if the heat exchange is taken into consideration, we obtain according to (3)

$$\dot{S}(\mathbf{Z}) = \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e + \Sigma. \quad (15)$$

Here,  $\dot{Q}$  and  $\dot{\mathbf{n}}^e$  are the exchange quantities,  $s$  the molar entropies, whereas  $\Sigma$  is the *entropy production* which is not negative according to the *Second Law*

$$\Sigma \geq 0 \longrightarrow \dot{S} \geq \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e \longrightarrow 0 \geq \oint \left[ \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e \right] dt. \quad (16)$$

State functions on a large state space  $\mathcal{Z}$  [13] are unique, and if the considered Schottky system is adiabatically unique [18], the entropy rate  $\dot{S}$  is the time derivative of a state space function entropy  $S(\mathbf{Z})$  according to (6). Consequently, its integration along a cyclic process vanishes, resulting in Clausius' inequality (16)<sub>3</sub>. Because  $S$  is a non-equilibrium entropy, also the temperature  $\Theta$ , the molar entropies and the entropy production in (15) are non-equilibrium quantities.<sup>7</sup> The non-equilibrium temperature  $\Theta$  is the contact temperature which is detailed considered in Sect. 4.2.

Presupposing that all chemical components in  $\mathcal{G}$  have the same temperature  $\Theta$ , the non-equilibrium molar entropies  $s$  in (15) are [19]

$$s = \frac{1}{\Theta} (\mathbf{h} - \boldsymbol{\mu}), \quad (17)$$

with the non-equilibrium molar enthalpies  $\mathbf{h}$  appearing in the First Law (11) and the non-equilibrium chemical potentials  $\boldsymbol{\mu}$ . For the present, these non-equilibrium quantities  $(\Theta, \mathbf{h}, \boldsymbol{\mu})$  are unknown and only place-holders which will be determined in Sect. 4.2. Consequently taking (11) and (17) into account, the entropy time rate (15) becomes

$$\dot{S} = \frac{1}{\Theta} \left( \dot{U} - \mathbf{A} \cdot \dot{\mathbf{a}} - \boldsymbol{\mu} \cdot \dot{\mathbf{n}}^e \right) + \Sigma. \quad (18)$$

Because the external mole number rates  $\dot{\mathbf{n}}^e$  are no state variables,<sup>8</sup> but the mole numbers themselves are included in the equilibrium subspace (6)<sub>1</sub> according to the Zeroth Law, the missing term for generating the mole numbers in (18) is hidden in the entropy production

$$\Sigma = -\frac{1}{\Theta} \boldsymbol{\mu} \cdot \dot{\mathbf{n}}^i + \Sigma^0, \quad (19)$$

and (18) results in

$$\dot{S}(\mathbf{Z}) = \frac{1}{\Theta} \left( \dot{U} - \mathbf{A} \cdot \dot{\mathbf{a}} - \boldsymbol{\mu} \cdot \dot{\mathbf{n}} \right) + \Sigma^0, \quad \Sigma^0 \geq 0, \quad (20)$$

if the internal mole number changing due to chemical reactions

$$\dot{\mathbf{n}}^i = \dot{\mathbf{n}} - \dot{\mathbf{n}}^e \quad (21)$$

are taken into account. Because the bracket in (20) contains only rates of equilibrium variables, those of the non-equilibrium state variables appear in the entropy production  $\Sigma^0$  which is established in Sect. 4.4.

<sup>6</sup> About the existence of a "non-equilibrium" entropy see [5].

<sup>7</sup> If  $\Theta$  is replaced in (15) by the thermostatic temperature  $T^\square$  of the environment,  $\dot{S}$  is not a time derivative of a state function because  $T^\square$  does not belong to the Schottky system and (16)<sub>3</sub> is not valid.

<sup>8</sup> Because they depend on the environment.

### 3.4 Reversible and accompanying processes

A reversible "process" is defined as a trajectory on the *equilibrium subspace*  $\Omega$  (6)<sub>1</sub> along that the entropy production (19) vanishes by definition

$$\Sigma^* = -\frac{1}{T^*} \boldsymbol{\mu}^* \cdot \dot{\mathbf{n}}^{i*} + \Sigma^{0*} \equiv 0, \quad \dot{\mathbf{n}}^{i*} \equiv 0, \quad (22)$$

because chemical reactions are irreversible processes. The entropy rate (15) of a reversible process is

$$\dot{S}^* := \frac{1}{T^*} \dot{Q}^* + s^* \cdot \dot{\mathbf{n}}^{e*}, \quad \Sigma^* \equiv 0, \quad (23)$$

and (20) results in

$$\dot{S}^* = \frac{1}{T^*} \left( \dot{U}^* - \mathbf{A}^* \cdot \dot{\mathbf{a}}^* - \boldsymbol{\mu}^* \cdot \dot{\mathbf{n}}^* \right), \quad \Sigma^{0*} \equiv 0. \quad (24)$$

The First Law of reversible processes is according to (11)

$$\dot{U}^* = \dot{Q}^* + \mathbf{h}^* \cdot \dot{\mathbf{n}}^{e*} + \dot{W}^* = \dot{Q}^* + \mathbf{h}^* \cdot \dot{\mathbf{n}}^* + \mathbf{A}^* \cdot \dot{\mathbf{a}}^*, \quad \dot{\mathbf{n}}^{i*} \equiv 0. \quad (25)$$

Special reversible processes are generated by projections (9) of an irreversible process  $\mathbf{Z}(t)$  onto the equilibrium subspace: the accompanying processes  $\mathcal{P}\mathbf{Z}(t)$ ,<sup>9</sup>

$$\dot{U}^* \doteq \dot{U}, \quad \dot{\mathbf{a}}^* \doteq \dot{\mathbf{a}}, \quad \dot{\mathbf{n}}^* \doteq \dot{\mathbf{n}}, \quad (26)$$

resulting in the First Law and the entropy time rate of accompanying processes

$$\dot{U} = \dot{Q}^* + \mathbf{h}^* \cdot \dot{\mathbf{n}} + \mathbf{A}^* \cdot \dot{\mathbf{a}}, \quad \dot{S}^*(\Omega) = \frac{1}{T^*} \left( \dot{U} - \mathbf{A}^* \cdot \dot{\mathbf{a}} - \boldsymbol{\mu}^* \cdot \dot{\mathbf{n}} \right). \quad (27)$$

The connection between the non-equilibrium quantities  $(\Theta, \dot{Q}, s, \mathbf{h}, \boldsymbol{\mu}, \mathbf{A}, \dot{S})$  and the projected equilibrium quantities  $(T^*, \dot{Q}^*, s^*, \mathbf{h}^*, \boldsymbol{\mu}^*, \mathbf{A}^*, \dot{S}^*)$  is investigated in Sect. 7.3.

## 4 Contact quantities

### 4.1 Defining inequalities

A discrete non-equilibrium system  $\mathcal{G}$  is now considered which is surrounded with an equilibrium reservoir  $\mathcal{G}^\square$  having a joint surface  $\partial\mathcal{G} \equiv \partial\mathcal{G}^\square$ , that means, a compound system  $\mathcal{G} \cup \mathcal{G}^\square$  is considered whose sub-systems have mutual exchanges of heat, power and material. Usually,  $\mathcal{G}^\square$  is denoted as the system's controlling environment. The joint surface represents the partition between the two sub-systems. Especially, inert partitions are considered which are defined as follows: An inert partition does not absorb or emit heat, power and material [18], described by the following equations [4, 12]

$$\dot{Q} = -\dot{Q}^\square, \quad \dot{W} = \mathbf{A} \cdot \dot{\mathbf{a}} = \mathbf{A}^\square \cdot \dot{\mathbf{a}} = -\dot{W}^\square, \quad \dot{\mathbf{n}}^e = -\dot{\mathbf{n}}^{\square e}. \quad (28)$$

The  $\square$ -quantities belong to the system's controlling environment  $\mathcal{G}^\square$ . The power done on the system is performed by the environment using its generalized forces  $\mathbf{A}^\square$  and related to the work variables of the system. The permeability of  $\partial\mathcal{G}$  to heat, power and material is described by (28).

Now, special compound systems are considered which satisfy the following

**Axiom:** The non-negative entropy time rate of the isolated compound system  $\mathcal{G}^\square \cup \mathcal{G}$  is the sum of the entropy time rates of the sub-systems.

<sup>9</sup>  $\doteq$  marks a setting.

Taking (28)<sub>1,3</sub> into account, the total entropy time rate of the isolated compound system  $\mathcal{G} \cup \mathcal{G}^\square$  is according to this axiom

$$\begin{aligned}\dot{S}^{tot} &:= \dot{S} + \dot{S}^\square = \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e + \frac{1}{T^\square} \dot{Q}^\square + s^\square \cdot \dot{\mathbf{n}}^{\square e} + \Sigma \\ &= \left( \frac{1}{\Theta} - \frac{1}{T^\square} \right) \dot{Q} + (s - s^\square) \cdot \dot{\mathbf{n}}^e + \Sigma \geq 0.\end{aligned}\quad (29)$$

Up to now,  $\Theta$  and  $s$  are place holders in the dissipation inequality (29)<sub>2</sub> for the unknown contact quantities temperature and molar entropies. Whereas  $\Sigma$  is the internal entropy production of the sub-system  $\mathcal{G}$  according to (15),  $(1/\Theta - 1/T^\square) \dot{Q}$  and  $(s - s^\square) \cdot \dot{\mathbf{n}}^e$  represent the entropy production of the heat and material exchanges between the sub-systems of the compound system. If the system is a reversible one ( $\Sigma = 0$ ), these exchanges have to be compatible with the dissipation inequality (29)<sub>2</sub>. Because heat and material exchanges are independent of each other because  $\dot{Q}$  is the conductive heat exchange as described in Sect. 3.2, the following *defining inequalities* [5, 18]

$$\left( \frac{1}{\Theta} - \frac{1}{T^\square} \right) \dot{Q} \stackrel{*}{\geq} 0, \quad (s - s^\square) \cdot \dot{\mathbf{n}}^e \stackrel{*}{\geq} \mathbf{0}, \quad (\text{for each component}) \quad (30)$$

are demanded for defining the place holders *contact temperature*  $\Theta$  and *non-equilibrium molar entropies*  $s$  which now are ascribed to the sub-system  $\mathcal{G}$  of the compound system  $\mathcal{G}^\square \cup \mathcal{G}$  [9–11, 18]. As outlined in Sect. 4.2, the contact quantities  $\Theta$  and  $s$  are uniquely defined by the zeros of the inequalities caused by the zeros with change of sign of  $\dot{Q}$  and  $\dot{\mathbf{n}}^e$ .

In more detail: the non-equilibrium Schottky system  $\mathcal{G}$  is in contact with a thermally homogeneous equilibrium environment  $\mathcal{G}^\square$  of the thermostatic temperature  $T^\square$  and the molar equilibrium entropies  $s^\square$ . All chemical components in  $\mathcal{G}^\square$  have the same temperature  $T^\square$ . Then the inequalities (30) define the contact temperature  $\Theta$  and the molar entropies  $s$  as is demonstrated in the next section.

#### 4.2 Contact temperature, neq-enthalpy and chemical potential

Taking (17) into account for equilibrium and non-equilibrium processes, the defining inequality (30)<sub>2</sub> of the molar entropies can be satisfied, if the additional inequalities for the molar enthalpies and for the chemical potentials are demanded

$$\left( \frac{h}{\Theta} - \frac{h^\square}{T^\square} \right) \cdot \dot{\mathbf{n}}^e \stackrel{*}{\geq} 0, \quad \left( \frac{\mu^\square}{T^\square} - \frac{\mu}{\Theta} \right) \cdot \dot{\mathbf{n}}^e \stackrel{*}{\geq} 0. \quad (31)$$

Because the system's environment  $\mathcal{G}^\square$  is an equilibrium system, the quantities  $\boxplus^\square$  are well known. As already performed in the introduction, also the non-equilibrium quantities—temperature, molar enthalpies and chemical potentials—should be measurable quantities and not only being defined by arithmetical items. This measurability is guaranteed by special chosen environments  $\mathcal{G}^\square$  of  $\mathcal{G}$ , as demonstrated below.

Special equilibrium environments are considered which cause that certain non-equilibrium contact rates vanish

$$\mathcal{G}_\circ^\square : \dot{Q}_\circ = 0, \longrightarrow \Theta = T_\circ^\square, \quad \text{according to (30)}_1, \quad (32)$$

$$\mathcal{G}_{nj}^\square : \dot{n}_j^e = 0, \longrightarrow h_j = \frac{\Theta}{T^\square} h_j^\square, \quad \mu_j = \frac{\Theta}{T^\square} \mu_j^\square, \quad \text{according to (31)}. \quad (33)$$

For deriving (32)<sub>2</sub> and (33)<sub>2,3</sub> from (30)<sub>1</sub> and (31), the following proposition [20] is used:

$$f(\mathbf{X}) \cdot \mathbf{X} \geq \mathbf{0} \text{ (for all } \mathbf{X} \wedge f \text{ continuous at } \mathbf{X} = \mathbf{0}) \implies f(\mathbf{0}) = \mathbf{0}. \quad (34)$$

Consequently, the non-equilibrium contact quantities *contact temperature*  $\Theta$ , *molar non-equilibrium enthalpies*  $h$  and *non-equilibrium chemical potentials*  $\mu$  are defined by equilibrium quantities of special contacting equilibrium environments according to (32) and (33). In more detail:

According to (32), the following definition is made [9, 10, 21]

**Definition** The system's contact temperature  $\Theta$  is that thermostatic temperature  $T_{\ominus}^{\square}$  of the system's equilibrium environment for which the net heat exchange  $\dot{Q}_{\ominus}$  between the system and this environment through an inert partition vanishes by change of sign.

Corresponding definitions are valid for the non-equilibrium molar enthalpies and chemical potentials according to (33).

#### 4.3 The extended Clausius inequality

Presupposing that the non-equilibrium entropy  $S(\mathbf{Z})$  is a state function on the non-equilibrium state space (6)<sub>2</sub>,<sup>10</sup> the inequality (16)<sub>3</sub> is valid

$$0 \geq \oint \left[ \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e \right] dt \quad (35)$$

which can be denoted as *extended Clausius inequality* because it has the shape of the well-known Clausius inequality in which temperature and molar entropies of the equilibrium environment are replaced by the corresponding non-equilibrium quantities of the system. The usual Clausius inequality can be derived by taking the defining inequalities (30) into account

$$\frac{1}{\Theta} \dot{Q} \geq \frac{1}{T^{\square}} \dot{Q}, \quad s \cdot \dot{\mathbf{n}}^e \geq s^{\square} \cdot \dot{\mathbf{n}}^e \quad (36)$$

by which (35) can be estimated resulting in Clausius' inequality (37)<sub>2</sub>

$$0 \geq \oint \left[ \frac{1}{\Theta} \dot{Q} + s \cdot \dot{\mathbf{n}}^e \right] dt \geq \oint \left[ \frac{1}{T^{\square}} \dot{Q} + s^{\square} \cdot \dot{\mathbf{n}}^e \right] dt \quad (37)$$

Or in words:

**Proposition** If the non-equilibrium entropy is a state function on the non-equilibrium state space  $(\mathbf{a}, \mathbf{n}, U, \Theta, \xi)$ , and if the place-holders  $\Theta$  and  $s$  are identified as contact temperature and non-equilibrium molar entropies by the defining inequalities (36), the inequality (35) changes into the extended Clausius inequality by which the usual Clausius inequality (37)<sub>2</sub> can be derived.

Besides the exchange quantities  $\dot{Q}$  and  $\dot{\mathbf{n}}^e$ , the extended Clausius inequality contains quantities which belong to the Schottky system— $\Theta$  and  $s$ —which are replaced by quantities of the environment— $T^{\square}$  and  $s^{\square}$ —in the usual Clausius inequality.

#### 4.4 Internal energy and contact temperature

As easy to demonstrate, contact temperature  $\Theta$  and internal energy  $U$  are independent of each other in non-equilibrium. For this purpose, a rigid partition  $\partial \mathcal{G} (\dot{\mathbf{a}} \equiv \mathbf{0})$  between the Schottky system  $\mathcal{G}$  and its equilibrium environment  $\mathcal{G}^{\square}$  is chosen which is impervious to matter ( $\dot{\mathbf{n}}^e \equiv \mathbf{0}$ ) and a time-dependent environment temperature  $T^{\square}(t)$  which is always set equal to the value of the momentary contact temperature  $\Theta(t)$  of  $\mathcal{G}$ , resulting according to (30) and (11) in

$$T^{\square}(t) \stackrel{*}{=} \Theta(t) \longrightarrow \dot{Q} = 0 \longrightarrow \dot{U} = 0. \quad (38)$$

Because  $\Theta$  is time-dependent and  $U$  is constant, totally different from thermostatics, both quantities are independent of each other.

Because the contact temperature is independent of the internal energy, it represents an additional variable in (20) which is included in  $\Sigma^0$ . The choice of further non-equilibrium variables depends on the system in

<sup>10</sup> More details in Sect. 7.



consideration. Here, *internal variables*  $\xi$  are chosen because they allow a great flexibility of describing non-equilibria [22,23]. Consequently, the created non-equilibrium state space and the entropy production caused by the contact temperature and the internal variables are

$$\mathbf{Z} = (\mathbf{a}, \mathbf{n}, U, \Theta, \xi), \quad \Sigma^0 = \alpha \dot{\Theta} + \beta \cdot \dot{\xi} \geq 0. \quad (39)$$

According to (9), the corresponding equilibrium subspace is spanned by

$$\mathcal{P}\mathbf{Z} = \mathcal{P}(\mathbf{a}, \mathbf{n}, U, \Theta, \xi) = (\mathbf{a}, \mathbf{n}, U, \Theta(\mathbf{a}, \mathbf{n}, U), \xi(\mathbf{a}, \mathbf{n}, U)) = (\mathbf{\Omega}, \Theta(\mathbf{\Omega}), \xi(\mathbf{\Omega})). \quad (40)$$

By use of these state spaces in connection with the entropy production generated by the contact temperature and the internal variables, different stages of thermodynamics are introduced in Sect. 8.

### 5 Example: environmental controlled processes

We consider a closed non-equilibrium system without chemical reactions ( $\dot{\mathbf{n}} = \mathbf{0}$ ) whose contact temperature  $\Theta$  is the only non-equilibrium variable.<sup>11</sup> According to (39), the corresponding state space is

$$\mathbf{Z} = (\mathbf{a}, U, \Theta), \quad \Sigma^0 = \alpha \dot{\Theta} \geq 0. \quad (41)$$

First and Second Laws are

$$\dot{U} = \dot{Q} + \dot{W}, \quad \dot{S} = \frac{\dot{Q}}{\Theta} + \alpha \dot{\Theta}. \quad (42)$$

The exchange quantities  $\dot{Q}$  and  $\dot{W}$  are controlled by the system's environment of thermostatic temperature  $T^\square$ . The defining inequality (30)<sub>1</sub> gives rise to introduce the following nonlinear constitutive equation of the heat exchange

$$\dot{Q} = (T^\square - \Theta)\kappa, \quad \kappa = \mathcal{K}[T^\square - \Theta] \geq 0. \quad (43)$$

The time derivative is

$$\partial_t \dot{Q} = (\dot{T}^\square - \dot{\Theta})\kappa + (T^\square - \Theta) \left( \frac{\partial \mathcal{K}}{\partial T^\square} \dot{T}^\square + \frac{\partial \mathcal{K}}{\partial \Theta} \dot{\Theta} \right) \quad (44)$$

or

$$\begin{aligned} \kappa \partial_t \dot{Q} &= (\dot{T}^\square - \dot{\Theta})\kappa^2 + \dot{Q} \left( \frac{\partial \mathcal{K}}{\partial T^\square} \dot{T}^\square + \frac{\partial \mathcal{K}}{\partial \Theta} \dot{\Theta} \right) \\ &= \dot{T}^\square \left( \kappa^2 + \dot{Q} \frac{\partial \mathcal{K}}{\partial T^\square} \right) + \dot{\Theta} \left( \dot{Q} \frac{\partial \mathcal{K}}{\partial \Theta} - \kappa^2 \right), \end{aligned} \quad (45)$$

resulting in

$$\dot{\Theta} = \frac{\kappa \partial_t \dot{Q} - \dot{T}^\square \left( \kappa^2 + \dot{Q} \frac{\partial \mathcal{K}}{\partial T^\square} \right)}{\dot{Q} \frac{\partial \mathcal{K}}{\partial \Theta} - \kappa^2}, \quad (46)$$

an evolution equation of the contact temperature.

We now consider some special cases:

<sup>11</sup> A toy example for demonstrating the effectiveness of the contact temperature.

- Constant internal energy  $\rightarrow \dot{Q} = -\dot{W}$  according to (42)<sub>1</sub>. Although the internal energy is constant, the contact temperature is time-dependent

$$\dot{U} = 0 \rightarrow \dot{\Theta} = \frac{-\kappa \partial_t \dot{W} - \dot{T}^\square \left( \kappa^2 - \dot{W} \frac{\partial \mathcal{K}}{\partial T^\square} \right)}{-\dot{W} \frac{\partial \mathcal{K}}{\partial \Theta} - \kappa^2}. \quad (47)$$

- The thermostatic temperature  $T^\square$  of the system's environment is constant

$$\dot{T}^\square = 0 \rightarrow \dot{\Theta} = \frac{\kappa \partial_t \dot{Q}}{\dot{Q} \frac{\partial \mathcal{K}}{\partial \Theta} - \kappa^2}. \quad (48)$$

- The system is isolated

$$\dot{U} = 0 \wedge \dot{W} = 0 \wedge T^\square = \Theta \rightarrow \dot{\Theta} = \dot{\Theta}, \quad (49)$$

that means, if using the constitutive equation (43)<sub>1</sub> of pure heat conduction, the time development of the contact temperature in isolated systems is indeterminated. The reason for that is the fact that neither the constitutive equation (43) nor the state space (41)<sub>1</sub> contain internal variables which are necessary to extend this simple example.

Some remarks on internal variables are now necessary.

## 6 Brief view at internal variables

Historically, the concept of internal variables can be traced back to Bridgman [24], Meixner [25], Maugin [26] and many others. The introduction of internal variables makes possible to use large state spaces, that means, material properties can be described by mappings defined on the state space variables  $\mathbf{Z}$ , thus avoiding the use of their histories which appear in small state spaces [13, 14, 27]. Consequently, internal variables allow to use the methods of Irreversible and/or Extended Thermodynamics [28].

Internal variables cannot be chosen arbitrarily: there are seven concepts which restrict their introduction [22]. The most essential ones are:

- Internal variables need a model or an interpretation,
- Beyond the constitutive and balance equations, internal variables require rate equations which can be adapted to different situations, making the use of internal variables flexible and versatile,
- The time rates of the internal variables do not occur in the work differential of the First Law,
- An isolation of the discrete system does not influence the values of the internal variables,
- In equilibrium, the internal variables become dependent on the variables of the equilibrium subspace, if the equilibrium is unconstrained.

Satisfying these concepts, the internal variables entertain an ambiguous relationship with microstructure [23].

As the last term of (39) shows, internal variables must be complemented by an evolution law<sup>12</sup> which may have the shape

$$\dot{\xi} = \mathbf{f}(U, \mathbf{a}, \xi) + \mathbf{g}(U, \mathbf{a}, \xi) \dot{U} + \mathbf{h}(U, \mathbf{a}, \xi) \cdot \dot{\mathbf{a}}. \quad (50)$$

Special one-dimensional cases are

$$\text{relaxation type: } \dot{\xi}(t) = -\frac{1}{\tau(U, \mathbf{a}, \Theta)} (\xi(t) - \xi^{eq}), \quad (51)$$

$$\text{reaction type [22]: } \dot{\xi}(t) = \gamma(U, \mathbf{a}, \Theta) \left[ 1 - \exp(-\mu(t)\beta(U, \mathbf{a}, \Theta)) \right]. \quad (52)$$

<sup>12</sup> [28], 3.5, 4.7.B, [23]I, 4.

Clear is that the contact temperature  $\Theta$  and  $\xi$  are different types of internal variables [29]:  $\dot{\Theta}$  is entropy generating because the contact temperature is independent of the internal energy, and  $\dot{\xi}$  is entropy producing due to irreversible processes in the system  $\mathcal{G}$ . This difference allows to introduce a classification into stages of thermodynamics in Sect. 8.

## 7 Non-equilibrium entropy

### 7.1 Adiabatical uniqueness

Up to now, the projection of a non-equilibrium state  $\mathbf{Z}$  onto an equilibrium one  $\mathcal{P}\mathbf{Z}$  was formally introduced according to (40). Now, the physical meaning of  $\mathcal{P}$  is demonstrated in two steps: Consider an arbitrary non-equilibrium state marked by  $C$

$$\mathbf{Z}_C = (U_C, \mathbf{a}_C, \mathbf{n}_C, \Theta_C, \xi_C) \quad (53)$$

and two different processes both starting at  $\mathbf{Z}_C$

- (1) in an isolated system without chemical reactions

$$\mathcal{I} : \dot{U} = 0, \dot{\mathbf{a}} = \mathbf{0}, \dot{\mathbf{n}} = \mathbf{0}, \quad (54)$$

- (2) in an open system with chemical reactions

$$\mathcal{T} : \dot{U} = 0, \dot{\mathbf{a}} = \mathbf{0}, \dot{\mathbf{n}}^e = -\dot{\mathbf{n}}^i \longrightarrow \dot{\mathbf{n}} = \mathbf{0}, \quad (55)$$

$$\dot{U} = \dot{Q} + \mathbf{h} \cdot \dot{\mathbf{n}}^e + \dot{W} \longrightarrow \dot{Q} = \mathbf{h} \cdot \dot{\mathbf{n}}^i. \quad (56)$$

Now, the process #1 is considered: Presupposing that the isolated system is adiabatically unique [18]

**Definition** A Schottky system is called *adiabatically unique*, if for each arbitrary, but fixed non-equilibrium state  $C$  after isolation of the system the relaxation process ends always in the same final equilibrium state  $A_{eq}$ , independently of how the process into  $C$  was performed.

The entropy difference along  $\mathcal{I}$  is according to (20)<sub>1</sub>, (39)<sub>2</sub> and (54),

$$\begin{aligned} \mathcal{I} \int_C^{A_{eq}} \dot{S}(\mathbf{Z}) dt &= \mathcal{I} \int_C^{A_{eq}} (\alpha \dot{\Theta} + \beta \cdot \dot{\xi}) dt = S(\mathcal{P}\mathbf{Z}_C) - S(\mathbf{Z}_C) \\ &= S^*(\boldsymbol{\Omega}_{A_{eq}}) - S(\mathbf{Z}_C). \end{aligned} \quad (57)$$

Because of the same entropy production according to (55) and (56), the process #2 along  $\mathcal{T}$  results likewise in the same final equilibrium state  $A_{eq}$  although the process runs in an open system with chemical reactions

$$\mathcal{T} \int_C^{A_{eq}} \dot{S}(\mathbf{Z}) dt = \mathcal{T} \int_C^{A_{eq}} (\alpha \dot{\Theta} + \beta \cdot \dot{\xi}) dt = S^*(\boldsymbol{\Omega}_{A_{eq}}) - S(\mathbf{Z}_C). \quad (58)$$

Due to the adiabatical uniqueness,  $A_{eq}$  is clearly accessible from  $\mathbf{Z}_C$  and the entropy difference, (57) and (58), between them is independent of the system's closing. According to the projection (40), the equilibrium variables of the non-equilibrium state (53) are transferred to the equilibrium state

$$S(\mathcal{P}\mathbf{Z}_C) = S(U_C, \mathbf{a}_C, \mathbf{n}_C, \Theta(U_C, \mathbf{a}_C, \mathbf{n}_C), \xi(U_C, \mathbf{a}_C, \mathbf{n}_C)). \quad (59)$$

Vice versa, the equation (57)<sub>2</sub> can be interpreted as a definition of a non-equilibrium entropy [14]

$$S(\mathbf{Z}_C) := S^*(\boldsymbol{\Omega}_{A_{eq}}) - \mathcal{I} \int_C^{A_{eq}} (\alpha \dot{\Theta} + \beta \cdot \dot{\xi}) dt, \quad (60)$$

if the equilibrium entropy and the entropy production are known.

## 7.2 The embedding theorem

Now the entropy time rates are considered which follow from (60), that means, the non-equilibrium state  $\mathbf{Z}(\tau)$  and its projection onto the equilibrium subspace  $\mathcal{P}\mathbf{Z}(\tau)$  depend on the time  $\tau$ . If this time differentiation

$$\frac{d}{d\tau} \boxplus \equiv \check{\boxplus} \quad (61)$$

is introduced, (60) results in

$$\check{S}(\mathbf{Z})(\tau) = \check{S}(\mathcal{P}\mathbf{Z})(\tau) - \frac{d}{d\tau} \left[ \mathcal{I} \int_{\mathbf{Z}(\tau)}^{\mathcal{P}\mathbf{Z}(\tau)} \left( \alpha \dot{\Theta} + \beta \cdot \dot{\xi} \right) dt \right]. \quad (62)$$

The entropy difference between two equilibrium states  $Aeq$  and  $Beq$  is obtained by integration along an arbitrary process  $\mathcal{S}$  between them on the non-equilibrium space and along the corresponding reversible accompanying process  $\mathcal{R}$  on the equilibrium subspace

$$\begin{aligned} & \mathcal{S} \int_{Aeq}^{Beq} \check{S}(\mathbf{Z})(\tau) d\tau \\ &= \mathcal{R} \int_{Aeq}^{Beq} \check{S}(\mathcal{P}\mathbf{Z})(\tau) d\tau - \int_{Aeq}^{Beq} \left\{ \frac{d}{d\tau} \left[ \mathcal{I} \int_{\mathbf{Z}(\tau)}^{\mathcal{P}\mathbf{Z}(\tau)} \left( \alpha \dot{\Theta} + \beta \cdot \dot{\xi} \right) dt \right] \right\} d\tau. \end{aligned} \quad (63)$$

The last term of (63) results in

$$\begin{aligned} & \left[ \mathcal{I} \int_{\mathbf{Z}(\tau)}^{\mathcal{P}\mathbf{Z}(\tau)} \left( \alpha \dot{\Theta} + \beta \cdot \dot{\xi} \right) dt \right]_{Aeq}^{Beq} = 0, \\ & \text{because: } \mathcal{P}\mathbf{Z}_{Beq} = \mathbf{Z}_{Beq}, \quad \mathcal{P}\mathbf{Z}_{Aeq} = \mathbf{Z}_{Aeq}. \end{aligned} \quad (64)$$

Consequently, the *embedding theorem* is proven

$$\mathcal{S} \int_{Aeq}^{Beq} \dot{S}(\mathbf{Z})(t) dt = \mathcal{R} \int_{Aeq}^{Beq} \dot{S}(\mathcal{P}\mathbf{Z})(t) dt = S_{Beq}^* - S_{Aeq}^*, \quad (65)$$

stating that the time rate of a non-equilibrium entropy  $\dot{S}(\mathbf{Z})$  integrated along an irreversible process  $\mathcal{S}$  between two equilibrium states  $Aeq$  and  $Beq$  is equal to the integral of the "time rate" of the equilibrium entropy  $\dot{S}(\mathcal{P}\mathbf{Z})$  along the reversible accompanying process  $\mathcal{R}$ . The embedding theorem ensures that the non-equilibrium entropy is compatible with the corresponding equilibrium entropy, that means, non-equilibrium entropies have to be defined with respect to the accompanying equilibrium ones, as done by the definition (60).

## 7.3 Accompanying entropy time rate

Starting with the reversible "process" (40)

$$\mathcal{P}\mathbf{Z}(t) = \mathcal{P}(\mathbf{a}, \mathbf{n}, U, \Theta, \xi)(t) = (\mathbf{a}, \mathbf{n}, U, \Theta(\mathbf{a}, \mathbf{n}, U), \xi(\mathbf{a}, \mathbf{n}, U))(t) = (\mathbf{\Omega})(t) \quad (66)$$

which is the *accompanying process* belonging to  $\mathbf{Z}(t) = (\mathbf{a}, \mathbf{n}, U, \Theta, \xi)(t)$ , the corresponding entropy time rates are according to (20), (39)<sub>2</sub> and (66)<sub>2</sub>

$$\dot{S}(\mathbf{Z}) = \frac{1}{\Theta} \left( \dot{U} - \mathbf{A}(\mathbf{Z}) \cdot \dot{\mathbf{a}} - \mu(\mathbf{Z}) \cdot \dot{\mathbf{n}} \right) + \alpha(\mathbf{Z}) \dot{\Theta} + \beta(\mathbf{Z}) \cdot \dot{\xi}, \quad (67)$$

$$\begin{aligned} \dot{S}(\mathcal{P}\mathbf{Z}) &= \frac{1}{\Theta(\Omega)} \left( \dot{U} - \mathbf{A}(\Omega) \cdot \dot{\mathbf{a}} - \mu(\Omega) \cdot \dot{\mathbf{n}} \right) + \alpha(\Omega) \dot{\Theta}(\Omega) + \beta(\Omega) \cdot \dot{\xi}(\Omega) \\ &= \left( \frac{1}{\Theta(\Omega)} + \alpha(\Omega) \frac{\partial \Theta}{\partial U} + \beta(\Omega) \cdot \frac{\partial \xi}{\partial U} \right) \dot{U} \\ &\quad - \left( \frac{\mathbf{A}(\Omega)}{\Theta(\Omega)} - \alpha(\Omega) \frac{\partial \Theta}{\partial \mathbf{a}} - \beta(\Omega) \cdot \frac{\partial \xi}{\partial \mathbf{a}} \right) \cdot \dot{\mathbf{a}} \\ &\quad - \left( \frac{\mu(\Omega)}{\Theta(\Omega)} - \alpha(\Omega) \frac{\partial \Theta}{\partial \mathbf{n}} - \beta(\Omega) \cdot \frac{\partial \xi}{\partial \mathbf{n}} \right) \cdot \dot{\mathbf{n}} \\ &\equiv \dot{S}^*(\Omega) = \frac{1}{T^*} \left( \dot{U} - \mathbf{A}^* \cdot \dot{\mathbf{a}} - \mu^* \cdot \dot{\mathbf{n}} \right), \end{aligned} \quad (68)$$

resulting in

$$\frac{1}{T^*} = \frac{1}{\Theta(\Omega)} + \alpha(\Omega) \frac{\partial \Theta}{\partial U} + \beta(\Omega) \cdot \frac{\partial \xi}{\partial U}, \quad | \dot{U} \quad (69)$$

$$\frac{\mathbf{A}^*}{T^*} = \frac{\mathbf{A}(\Omega)}{\Theta(\Omega)} - \alpha(\Omega) \frac{\partial \Theta}{\partial \mathbf{a}} - \beta(\Omega) \cdot \frac{\partial \xi}{\partial \mathbf{a}}, \quad | - \dot{\mathbf{a}} \quad (70)$$

$$\frac{\mu^*}{T^*} = \frac{\mu(\Omega)}{\Theta(\Omega)} - \alpha(\Omega) \frac{\partial \Theta}{\partial \mathbf{n}} - \beta(\Omega) \cdot \frac{\partial \xi}{\partial \mathbf{n}}, \quad | - \dot{\mathbf{n}}. \quad (71)$$

The entropy time rate of the original irreversible process is (67), that of the accompanying process generated by projection (66) is (68). The entropy rate of the accompanying process (68) has two different, but equivalent representations: one defined on the space  $\mathcal{P}\mathbf{Z}$ , the other one is defined on the equilibrium subspace  $\Omega$ . Multiplying (69) to (71) as specified and summing up, results as expected in (68)<sub>3</sub>

$$\dot{S}^*(\Omega) = \dot{S}(\mathcal{P}\mathbf{Z}) \quad (72)$$

and demonstrates that the entropy production of an accompanying process vanishes.

## 8 Thermodynamical stages of Schottky systems

### 8.1 The stage of contact quantities

The general case is characterized by processes on the non-equilibrium state space (39)<sub>1</sub> for which contact temperature and internal energy are independent state variables. The time rate of the non-equilibrium entropy (67) results in the integrability conditions

$$\frac{\partial S(\mathbf{Z})}{\partial U} = \frac{1}{\Theta}, \quad \frac{\partial S(\mathbf{Z})}{\partial \mathbf{a}} = -\frac{\mathbf{A}}{\Theta}, \quad \frac{\partial S(\mathbf{Z})}{\partial \mathbf{n}} = -\frac{\mu}{\Theta}, \quad (73)$$

$$\frac{\partial S(\mathbf{Z})}{\partial \Theta} = \alpha, \quad \frac{\partial S(\mathbf{Z})}{\partial \xi} = \beta. \quad (74)$$

Because  $\Theta$  and  $U$  are independent of each other according to (38), (73)<sub>1</sub> can be integrated immediately

$$S(U, \mathbf{a}, \mathbf{n}, \Theta, \xi) = \frac{1}{\Theta} U + K(\mathbf{a}, \mathbf{n}, \Theta, \xi). \quad (75)$$

Consequently, the non-equilibrium entropy is a linear function of the internal energy. Here

$$-\Theta K = F(\mathbf{a}, \mathbf{n}, \Theta, \xi) \quad (76)$$

is the free energy  $F$ . From the integrability conditions (73) and (74) follow that except of  $\alpha$ , all constitutive equations do not depend on the internal energy  $U$ , but instead on the contact temperature:

$$\frac{\partial}{\partial \mathbf{a}} \frac{\partial S}{\partial U} = \mathbf{0} \implies \frac{\partial \mathbf{A}}{\partial U} = \mathbf{0}, \quad (77)$$

$$\frac{\partial}{\partial \mathbf{n}} \frac{\partial S}{\partial U} = \mathbf{0} \implies \frac{\partial \boldsymbol{\mu}}{\partial U} = \mathbf{0}, \quad (78)$$

$$\frac{\partial}{\partial \boldsymbol{\xi}} \frac{\partial S}{\partial U} = \mathbf{0} \implies \frac{\partial \boldsymbol{\beta}}{\partial U} = \mathbf{0}, \quad (79)$$

$$\frac{\partial}{\partial \Theta} \frac{\partial S}{\partial U} = -\frac{1}{\Theta^2} = \frac{\partial \alpha}{\partial U} \implies \alpha = -\frac{U}{\Theta^2} + L(\mathbf{a}, \mathbf{n}, \Theta, \boldsymbol{\xi}). \quad (80)$$

Differentiating (75) and comparison with (73) and (74) results for the free energy (76) in

$$\frac{\partial F}{\partial \Theta} = -S - \Theta \alpha, \quad \frac{\partial F}{\partial \mathbf{a}} = \mathbf{A}, \quad \frac{\partial F}{\partial \mathbf{n}} = \boldsymbol{\mu}, \quad \frac{\partial F}{\partial \boldsymbol{\xi}} = -\Theta \boldsymbol{\beta}. \quad (81)$$

According to (80)<sub>3</sub>, the constitutive mapping  $\alpha$  is linear in the internal energy as well as the non-equilibrium entropy (75).

## 8.2 The endoreversible stage

The endoreversible case is characterized by "processes" on the equilibrium subspace (40) which are projections of real running processes (67). For these reversible accompanying processes, the contact temperature and the internal variables depend on the equilibrium variables. Consequently, the (contact) temperature depends on the internal energy. Because of the endoreversibility, there are no internal variables. This situation corresponds to the hypothesis of local equilibrium in the field formulation of thermodynamics.

The time rate of the entropy (68)<sub>4</sub>

$$\dot{S}^*(\boldsymbol{\Omega}) = \frac{1}{T^*} \left( \dot{U} - \mathbf{A}^* \cdot \dot{\mathbf{a}} - \boldsymbol{\mu}^* \cdot \dot{\mathbf{n}} \right), \quad \mathbf{A}^* := \mathbf{A}(\boldsymbol{\Omega}), \quad \boldsymbol{\mu}^* := \boldsymbol{\mu}(\boldsymbol{\Omega}) \quad (82)$$

results in the usual integrability conditions

$$\frac{\partial S(\boldsymbol{\Omega})}{\partial U} = \frac{1}{T^*}, \quad \frac{\partial S(\boldsymbol{\Omega})}{\partial \mathbf{a}} = -\frac{\mathbf{A}^*}{T^*}, \quad \frac{\partial S(\boldsymbol{\Omega})}{\partial \mathbf{n}} = -\frac{\boldsymbol{\mu}^*}{T^*} \quad (83)$$

whose RHSs are given by (69) to (71), if the stage of contact quantities is taken as a background description.

The entropy production along  $\mathcal{P}\mathbf{Z}(t)$  vanishes, the considered Schottky system undergoes a reversible accompanying process. Entropy production occurs, if different such Schottky systems interact with each other: the endoreversible case of finite time thermodynamics [30].

Because there exist irreversible processes making use of a temperature which depends on the internal energy, a third stage of thermodynamics has to be formulated in the next section.

## 8.3 The stage of thermal physics and engineering

Considering the independence of the contact temperature  $\Theta$  of the internal energy  $U$  as treated in Sect. 4.4, the entropy time rate of an irreversible process is given by (67) and that of its (reversible) accompanying process by (68). The entropy itself has the shape (75). Especially in thermal engineering, a temperature is used which is connected with the internal energy and which is different from the thermostatic temperature (69) of the accompanying process. A projection  $\mathcal{P}^+$  which suppresses the independence of the contact temperature of the internal energy is

$$\mathcal{P}^+ \mathbf{Z}(t) = \left( \mathbf{a}, \mathbf{n}, U, \Theta(\mathbf{a}, \mathbf{n}, U, \boldsymbol{\xi}), \boldsymbol{\xi} \right)(t) = \left( \mathbf{a}, \mathbf{n}, U, \boldsymbol{\xi} \right)(t) \equiv (\boldsymbol{\Omega}^+)(t). \quad (84)$$

A physical interpretation is as follows: the contact temperature loses its status as an independent variable, replacing it by a function of the equilibrium and of the internal variables defined on the non-equilibrium

state space (84)<sub>3</sub> which represents an intermediate concept of the non-equilibrium state space (39)<sub>1</sub> and the equilibrium subspace (66).

The entropy production (39)<sub>2</sub> becomes on  $\Omega^+$

$$\Sigma^+ = \beta^+ \cdot \dot{\xi} \quad (85)$$

because  $\Theta$  is not a state variable of  $\Omega^+$ , but a constitutive equation according to (84)<sub>1</sub>.

Analogously to (67) and (68), the time rate of the corresponding non-equilibrium entropy is

$$\begin{aligned} \dot{S}^+(\mathcal{P}^+\mathbf{Z}) &= \left( \frac{1}{\Theta(\Omega^+)} + \alpha(\Omega^+) \frac{\partial \Theta}{\partial U} \right) \dot{U} - \left( \frac{\mathbf{A}(\Omega^+)}{\Theta(\Omega^+)} - \alpha(\Omega^+) \frac{\partial \Theta}{\partial \mathbf{a}} \right) \cdot \dot{\mathbf{a}} \\ &\quad - \left( \frac{\boldsymbol{\mu}(\Omega^+)}{\Theta(\Omega^+)} - \alpha(\Omega^+) \frac{\partial \Theta}{\partial \mathbf{n}} \right) \cdot \dot{\mathbf{n}} + \left( \beta(\Omega^+) + \alpha(\Omega^+) \frac{\partial \Theta}{\partial \xi} \right) \cdot \dot{\xi} \end{aligned} \quad (86)$$

$$= \frac{1}{T^+} \left( \dot{U} - \mathbf{A}^+ \cdot \dot{\mathbf{a}} - \boldsymbol{\mu}^+ \cdot \dot{\mathbf{n}} \right) + \beta^+ \cdot \dot{\xi} =: \dot{S}^+(U, \mathbf{a}, \mathbf{n}, \xi), \quad (87)$$

resulting in

$$\frac{1}{T^+} := \frac{1}{\Theta(\Omega^+)} + \alpha(\Omega^+) \frac{\partial \Theta}{\partial U} = \frac{\partial S^+(\Omega^+)}{\partial U}, \quad (88)$$

$$\frac{\mathbf{A}^+}{T^+} := \frac{\mathbf{A}(\Omega^+)}{\Theta(\Omega^+)} - \alpha(\Omega^+) \frac{\partial \Theta}{\partial \mathbf{a}} = - \frac{\partial S^+(\Omega^+)}{\partial \mathbf{a}}, \quad (89)$$

$$\frac{\boldsymbol{\mu}^+}{T^+} := \frac{\boldsymbol{\mu}(\Omega^+)}{\Theta(\Omega^+)} - \alpha(\Omega^+) \frac{\partial \Theta}{\partial \mathbf{n}} = - \frac{\partial S^+(\Omega^+)}{\partial \mathbf{n}}, \quad (90)$$

$$\beta^+ := \beta(\Omega^+) + \alpha(\Omega^+) \frac{\partial \Theta}{\partial \xi} = \frac{\partial S^+(\Omega^+)}{\partial \xi}. \quad (91)$$

Considering a relaxation process  $\mathcal{I}$  (54) or  $\mathcal{T}$  (55) along which the equilibrium variables are fixed, the corresponding time rate of the non-equilibrium entropy (87) is equal to the entropy production, and the intensive variables (88) to (91) depend on the internal variables. Especially, the temperature (88) is defined on  $\Omega^+$  as a constitutive equation

$$T^+ = \vartheta^+(U, \mathbf{a}, \mathbf{n}, \xi) \quad (92)$$

as well as

$$\mathbf{A}^+(U, \mathbf{a}, \mathbf{n}, \xi), \quad \boldsymbol{\mu}^+(U, \mathbf{a}, \mathbf{n}, \xi), \quad \beta^+(U, \mathbf{a}, \mathbf{n}, \xi). \quad (93)$$

Now the following question is investigated: What are the conditions by which the non-equilibrium temperature (92) can be replaced by the thermostatic equilibrium temperature which does not depend on the internal variables

$$T_0 = \vartheta_0(U, \mathbf{a}, \mathbf{n}) \quad (94)$$

although non-equilibrium is under consideration? The settings

$$\alpha \doteq 0, \quad \xi \doteq \mathbf{0} \quad (95)$$

trace back to the endoreversible case and are therefore no suitable conditions to satisfy (94). But if  $\beta^+$  does not depend on the internal energy, (91) and (88) yield

$$\beta^+ = \beta(\mathbf{a}, \mathbf{n}, \xi) \quad \longrightarrow \quad \frac{\partial^2 S^+(\Omega^+)}{\partial U \partial \xi} = \mathbf{0}, \quad (96)$$

$$\longrightarrow \quad \frac{\partial}{\partial \xi} \frac{1}{T^+} = \mathbf{0} \quad \longrightarrow \quad T^+ = \theta^+(U, \mathbf{a}, \mathbf{n}) =: T_0. \quad (97)$$

Consequently, the following statement is proven:

**Proposition** *If the entropy production on the stage of thermal engineering, described by internal variables, is independent of the internal energy, the non-equilibrium temperature does not depend on these internal variables and is therefore the thermostatic equilibrium temperature although non-equilibrium is in consideration.*

If the entropy production does not depend on the internal energy, the temperature on the stage of thermal engineering is an equilibrium quantity, whereas  $\mathbf{A}^+$  and  $\boldsymbol{\mu}^+$  are not. Consequently, the temperature can be used as in thermostatics, although the entropy production (85) does not vanish. This fact may be called *contact temperature reduction* ( $T^+ \rightarrow T_0$ ) which is the reason why in thermal engineering no problems arise by use of the temperature, that is why it can be introduced as a “primitive concept” only depending on the equilibrium variables,<sup>13</sup> and that is why the contact temperature was not uncovered earlier.

The thermodynamical stages of Schottky systems introduce an order of their different non-equilibrium descriptions: the processes of the three stages can be arranged:  $\boxplus \implies \boxminus$  means,  $\boxplus$  takes more dissipative parts of the process into account than  $\boxminus$ :

$$\mathbf{Z}(t) \implies \mathcal{P}^+\mathbf{Z}(t) \implies \mathcal{P}\mathbf{Z}(t). \quad (98)$$

According to (96)<sub>2</sub>, if using the thermostatic temperature, the non-equilibrium entropy of this stage has the shape

$$S^+(\boldsymbol{\Omega}^+) = D(U, \mathbf{a}, \mathbf{n}) + B(\mathbf{a}, \mathbf{n}, \boldsymbol{\xi}), \quad (99)$$

resulting in

$$\dot{S}^+(\boldsymbol{\Omega}^+) = \frac{\partial D}{\partial U} \dot{U} + \frac{\partial(D+B)}{\partial \mathbf{a}} \cdot \dot{\mathbf{a}} + \frac{\partial(D+B)}{\partial \mathbf{n}} \cdot \dot{\mathbf{n}} + \frac{\partial B}{\partial \boldsymbol{\xi}} \cdot \dot{\boldsymbol{\xi}}, \quad (100)$$

and as a comparison with (87) shows

$$\frac{1}{T_0} = \frac{\partial D}{\partial U}, \quad \frac{\mathbf{A}^+}{T_0} = -\frac{\partial(D+B)}{\partial \mathbf{a}}, \quad \frac{\boldsymbol{\mu}^+}{T_0} = -\frac{\partial(D+B)}{\partial \mathbf{n}}, \quad \boldsymbol{\beta}^+ = \frac{\partial B}{\partial \boldsymbol{\xi}}. \quad (101)$$

Besides the in time local properties which are investigated in the last sections, an in time global property, the dissipation inequality, is discussed in the next section.

## 9 Dissipation inequality

Starting with the embedding theorem (65) with (67) and (82) by taking the entropy production (39)<sub>2</sub> into account

$$\begin{aligned} S/\mathcal{R} \int_{A^*}^{B^*} [\dot{S}(\mathbf{Z}) - \dot{S}(\mathcal{P}\mathbf{Z})] dt &= 0 \\ &= S/\mathcal{R} \int_{A^*}^{B^*} \left[ \left( \frac{1}{\Theta} - \frac{1}{T^*} \right) \dot{U} - \left( \frac{\mathbf{A}}{\Theta} - \frac{\mathbf{A}^*}{T^*} \right) \cdot \dot{\mathbf{a}} - \left( \frac{\boldsymbol{\mu}}{\Theta} - \frac{\boldsymbol{\mu}^*}{T^*} \right) \cdot \dot{\mathbf{n}} + \Sigma^0 \right] dt, \end{aligned} \quad (102)$$

the dissipation inequality follows

$$S/\mathcal{R} \int_{A^*}^{B^*} \left[ \left( \frac{1}{\Theta} - \frac{1}{T^*} \right) \dot{U} - \left( \frac{\mathbf{A}}{\Theta} - \frac{\mathbf{A}^*}{T^*} \right) \cdot \dot{\mathbf{a}} - \left( \frac{\boldsymbol{\mu}}{\Theta} - \frac{\boldsymbol{\mu}^*}{T^*} \right) \cdot \dot{\mathbf{n}} \right] dt \leq 0. \quad (103)$$

This inequality does not contain any entropy as well as no entropy production (entropy-free thermodynamics) [5, 15, 31]: the original irreversible process is compared with its accompanying process.

Every equilibrium entropy has to be defined uniquely, that means process independently between two states of the chosen equilibrium subspace. If the considered system is adiabatically unique [18], to each equilibrium entropy non-equilibrium entropies can uniquely be constructed by use of the entropy production according to (60). By construction, these non-equilibrium entropies satisfy the embedding theorem (65) which represents a constraint (103) for the contact quantities. Here, the procedure is the other way round: the non-equilibrium process induces the thermostatic approximation by reversible accompanying processes.

Besides the dissipation inequality, the efficiency is an other in time global quantity which is discussed in the next section.

<sup>13</sup> An often ad-hoc presupposed condition called “local equilibrium”.



### 10 Efficiency of generalized cyclic processes

#### 10.1 Generalized cyclic processes

We consider a cyclic, power producing process of a closed discrete system which works between two heat reservoirs of constant thermostatic temperatures  $T_H^* > T_L^*$  ( $\boxplus^*$  means reservoir related). The time-dependent contact temperatures of the two contacts between the system and the reservoirs are  $\Theta_H$  and  $\Theta_L$ , the net heat exchanges per cycle through the two contacts  $H$  and  $L$  are  $Q_H^*$  and  $Q_L^*$ . Because a power producing cyclic process is considered, the net heat exchanges satisfy the following inequalities

$$Q_H^* < 0, \quad Q_L^* > 0, \quad 0 < Q_L^* < -Q_H^*. \tag{104}$$

The signs of the heat exchanges through the contacts may depend on time, that means, the reservoir  $L$  does not absorb heat for all times, but there are times for emitting heat. This behavior is different from that of a Carnot process and typical for *generalized cyclic processes* which satisfy

$$Q_{\boxtimes}^* = \oint \dot{Q}_{\boxtimes}^*(t) dt = \oint \left[ \dot{Q}_{\boxtimes}^{*+}(t) + \dot{Q}_{\boxtimes}^{*-}(t) \right] dt, \quad \boxtimes = H, L, \tag{105}$$

$$\dot{Q}_{\boxtimes}^{*+} \geq 0, \quad \dot{Q}_{\boxtimes}^{*-} \leq 0. \tag{106}$$

According to (104)<sub>3</sub>

$$0 < \oint \left[ \dot{Q}_L^{*+}(t) + \dot{Q}_L^{*-}(t) \right] dt < - \oint \left[ \dot{Q}_H^{*+}(t) + \dot{Q}_H^{*-}(t) \right] dt \tag{107}$$

is valid.

#### 10.2 The mean values

According to the defining inequality (30)<sub>1</sub>, we obtain for the closed system

$$\left( \frac{1}{T_{\boxtimes}^*} - \frac{1}{\Theta_{\boxtimes}^{\diamond}} \right) \dot{Q}_{\boxtimes}^{*\diamond} \geq 0, \quad \boxtimes = H, L, \quad \diamond = +, -. \tag{108}$$

Using the mean value theorem and (108),

$$\oint \left( \frac{\dot{Q}_{\boxtimes}^{*+}}{\Theta_{\boxtimes}^+} + \frac{\dot{Q}_{\boxtimes}^{*-}}{\Theta_{\boxtimes}^-} \right) dt = \frac{Q_{\boxtimes}^{*+}}{[\Theta_{\boxtimes}^+]} + \frac{Q_{\boxtimes}^{*-}}{[\Theta_{\boxtimes}^-]} \leq \oint \frac{1}{T_{\boxtimes}^*} \left( \dot{Q}_{\boxtimes}^{*+} + \dot{Q}_{\boxtimes}^{*-} \right) dt \tag{109}$$

is valid. The brackets  $[\boxplus]$  mark the mean value generated by the cyclic process

$$\frac{1}{[\Theta_{\boxtimes}^{\diamond}]} = \frac{1}{Q_{\boxtimes}^{*\diamond}} \oint \frac{\dot{Q}_{\boxtimes}^{*\diamond}}{\Theta_{\boxtimes}^{\diamond}} dt, \quad \boxtimes = H, L, \quad \diamond = +, -. \tag{110}$$

The extended Clausius inequality of closed systems (37) [32,33] (one contact, heat exchange system related)

$$\oint \frac{\dot{Q}(t)}{T^*} dt \leq \oint \frac{\dot{Q}(t)}{\Theta(t)} dt \leq 0 \tag{111}$$

the RHS becomes for the here considered generalized cycle process (two contacts, four reservoir-related heat exchanges, inert partitions)

$$\oint \left( \frac{\dot{Q}_H^{*+}}{\Theta_H^+} + \frac{\dot{Q}_H^{*-}}{\Theta_H^-} + \frac{\dot{Q}_L^{*+}}{\Theta_L^+} + \frac{\dot{Q}_L^{*-}}{\Theta_L^-} \right) dt \geq 0. \tag{112}$$

The inequality (109)<sub>2</sub> written down for the reservoir  $H$  results by use of (107)<sub>2</sub> in

$$\frac{Q_H^{*+}}{[\Theta_H^+]} + \frac{Q_H^{*-}}{[\Theta_H^-]} \leq \oint \frac{1}{T_H^*} (\dot{Q}_H^{*+} + \dot{Q}_H^{*-}) dt < 0. \quad (113)$$

Because of (104)<sub>1</sub>, the LHS of (113) can be transformed by the mean value procedure

$$\frac{Q_H^{*+}}{[\Theta_H^+]} + \frac{Q_H^{*-}}{[\Theta_H^-]} = \frac{Q_H^*}{[\Theta_H]} \leq \oint \frac{1}{T_H^*} (\dot{Q}_H^{*+} + \dot{Q}_H^{*-}) dt < 0, \quad (114)$$

and according to (105) and (104)<sub>1</sub>, (114)<sub>2</sub> results in

$$[\Theta_H] \leq T_H^*, \quad \text{if } dT_H^*/dt = 0. \quad (115)$$

The LHS of (109) yields in connection with  $\boxtimes \equiv H$  and (113)<sub>2</sub>

$$\oint \left( \frac{\dot{Q}_H^{*+}}{\Theta_H^+} + \frac{\dot{Q}_H^{*-}}{\Theta_H^-} \right) dt < 0. \quad (116)$$

Consequently, according to (112) and (104)<sub>2</sub>, the mean value theorem yields

$$0 < \oint \left( \frac{\dot{Q}_L^{*+}}{\Theta_L^+} + \frac{\dot{Q}_L^{*-}}{\Theta_L^-} \right) dt = \frac{Q_L^{*+}}{[\Theta_L^+]} + \frac{Q_L^{*-}}{[\Theta_L^-]} = \frac{Q_L^*}{[\Theta_L]}. \quad (117)$$

The inequality (109)<sub>2</sub> written down for the reservoir  $L$  results in

$$0 < \frac{Q_L^*}{[\Theta_L]} = \frac{Q_L^{*+}}{[\Theta_L^+]} + \frac{Q_L^{*-}}{[\Theta_L^-]} \leq \oint \frac{1}{T_L^*} (\dot{Q}_L^{*+} + \dot{Q}_L^{*-}) dt \quad (118)$$

from which follows

$$[\Theta_L] \geq T_L^*, \quad \text{if } dT_L^*/dt = 0. \quad (119)$$

The mean values (115) and (119) follow from (114) and (118)

$$[\Theta_{\boxtimes}] = Q_{\boxtimes}^* \left( \frac{[\Theta_{\boxtimes}^+][\Theta_{\boxtimes}^-]}{Q_{\boxtimes}^{*+}[\Theta_{\boxtimes}^-] + Q_{\boxtimes}^{*-}[\Theta_{\boxtimes}^+]} \right). \quad (120)$$

If the cyclic process is not a generalized one

$$Q_H^{*+} \equiv 0, \quad Q_H^{*-} \neq 0, \quad Q_L^{*+} \neq 0, \quad Q_L^{*-} \equiv 0, \quad (121)$$

the equations (114)<sub>1</sub> and (118)<sub>2</sub> become identities and (115) and (119) are still valid.

### 10.3 Efficiency

The Carnot efficiency is a statement less applying to generalized cyclic processes because it is only valid for reversible ordinary cyclic processes. Here, irreversible generalized cyclic processes (105) and (106) are considered and the thermostatic temperatures  $T_H^*$  and  $T_L^*$  of the controlling reservoirs can be estimated by the inequalities (115) and (119) introducing mean values of the generalized cyclic processes

$$\eta_{CAR} = 1 - \frac{T_L^*}{T_H^*} \geq 1 - \frac{[\Theta_L]}{[\Theta_H]} =: \eta_{gcp}. \quad (122)$$

Consequently, the smaller efficiency  $\eta_{gcp}$  is a more realistic measure for non-equilibrium processes than the Carnot efficiency  $\eta_{CAR}$  which belongs to reversible cyclic processes.

## 11 Summary

Discrete systems in non-equilibrium can be described by use of two different procedures: the endoreversible treatment [30] or considering the system's internal entropy production used in this paper. Establishing a non-equilibrium entropy means that also a non-equilibrium temperature has to be introduced according to (1) or (2). But then the question arises why in thermal physics and engineering temperature is introduced as a "primitive concept," that means, do not ask, if the used temperature is an equilibrium or a non-equilibrium quantity. Clear is, that in the endoreversible treatment temperature belongs to equilibrium because the systems themselves are in equilibrium. But also if the system is in non-equilibrium, temperature is used as a primitive concept or as an arithmetical quantity according to (1), not knowing, if a thermometer for a such theoretically defined quantity exists. However, in practice thermometers are used measuring temperatures without clarifying, if these belong to equilibrium or non-equilibrium, and why despite this vagueness thermal physics is so extraordinary successful? This and other questions are answered in the following steps:

- A directly measurable non-equilibrium temperature (30)<sub>1</sub>, the contact temperature and a non-equilibrium entropy (20) are introduced, defined as a state function on the non-equilibrium state space (39) spanned by internal energy, work variables, mole numbers, contact temperature and internal variables. Energy and temperature are for the present independent of each other in non-equilibrium. Considering a special material, they become dependent according to that material, such as they are dependent in equilibrium.
- Because internal energy and contact temperature are independent of each other, both have to be introduced as independent variables on the non-equilibrium state space.
- According to the First Law, the equilibrium subspace is spanned by internal energy, work variables and mole numbers, the non-equilibrium part by contact temperature and internal variables.
- Irreversible processes are described by trajectories on the non-equilibrium state space.
- Every non-equilibrium process generates by projection onto the equilibrium subspace a reversible accompanying "process" as a trajectory on the equilibrium subspace (40) with the slaved time as a path parameter.
- This projection procedure allows to define a non-equilibrium entropy (60), if the equilibrium entropy and the entropy production are known.
- Irreversible processes between two equilibrium states have to be compatible with the corresponding accompanying processes between the same equilibrium states. This evident property is guaranteed, if the considered system is adiabatically unique and the embedding theorem (65) is satisfied (Sect. 7).
- In equilibrium, the non-equilibrium variables—contact temperature and internal variables—are functions of the equilibrium variables—internal energy, work variables and mole numbers.
- The relaxation of the non-equilibrium variables to their equilibrium values allows to introduce three so-called thermodynamical stages (Sect. 8):
  - (i) The general case of contact quantities: the non-equilibrium variables are not relaxed.
  - (ii) The stage of thermal engineering: in general, the contact temperature depends on the internal variables, but if additionally the entropy production does not depend on the internal energy (satisfied for nearly all cases), the temperature depends only on the equilibrium variables  $T_0 = \Theta(U, \mathbf{a}, \mathbf{n})$ . Thus, its value  $T_0$  is the equilibrium temperature which in this case can be successfully used in non-equilibrium.
  - (iii) The endoreversible stage: All non-equilibrium variables are relaxed, the entropy production is zero, the processes in the sub-systems are reversible, and the entropy production is caused by irreversible processes between the sub-systems. This case corresponds to the hypothesis of "local equilibrium" in the field formulation of thermodynamics.
- The global dissipation inequality of entropy-free thermodynamics is revisited (Sect. 9).
- The contact temperature makes possible to define an efficiency which is smaller than that of the reversible Carnot process and which is valid for irreversible and more general cyclic processes. Thus, this efficiency is more realistic than that of Carnot.

Beside the introduction to non-equilibrium thermodynamics of Schottky systems, the main result consists in the answer of the question: Why can an equilibrium temperature successfully be used in irreversible thermal physics and engineering?

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